Appendix F

Overview of Rebound Test Procedures and Data Evaluation

F-1. Introduction

a. Purpose

This appendix lays out a theoretical and practical framework for the collection and evaluation of data during rebound testing. As mentioned in Section 9-9, rebound tests (also known as "pulsing tests") are commonly used to assess the attainment of cleanup in the vadose zone. However, little information is available to guide field practitioners through the data collection and its interpretation (Holbrook et al., 1998). The objective of this appendix is to fill this void by providing a step-by-step approach to planning and performing a rebound test along with straightforward mathematical techniques for evaluating the data to determine adequacy of cleanup. The material presented in this appendix is intended to be an introduction to rebound testing and serves as a practical starting point for further development of this important procedure.

b. Background

The intent of rebound testing is to assess residual contamination remaining in soils after a period of active remediation. The underlying premise is that soils are inherently heterogeneous and may often be divided into two relative categories: low permeability and high permeability. During soil vapor extraction, vapors flow predominantly in the high permeability soils intersected by extraction wells and contaminant removal is primarily from these soils. This extraction creates a difference, or gradient, in the concentration between more permeable and less permeable soils. Contaminants residing in the less permeable soils are removed only after migrating into more permeable soils where soil vapors are flowing (DiGiulio et al., 1998). The migration occurs primarily by vaporous diffusion into active flow paths caused by the concentration gradient. Similar contaminant transport occurs during bioventing. During a period of rebound (i.e., no extraction or injection), the soil vapors are relatively dormant and contaminant concentrations equilibrate between phases and soil types. In other words, the air is not moving and contaminant vapors diffuse from lesser to more permeable soils and the vapor concentration in the more permeable soils approaches that of the low permeability soils. The vapor concentration in the more permeable soils can be measured periodically in the extraction wells to track the progress of rebound. Hence, the goal of a rebound test is to measure the concentration remaining in the least permeable soils by allowing equilibration of contaminant vapors among all soil types at a site. A measure of the concentration in less permeable soils is a strong indicator of the residual contamination at the site.

c. Introductory Example

Consider an SVE site with a single extraction well in the middle of a vapor plume within which no NAPL exists. Assume a uniform extraction rate has been drawn from the well since the initiation of operation except for two periods of dormancy. Measurements of the vapor concentration within the extraction well are illustrated in Figure F-1.

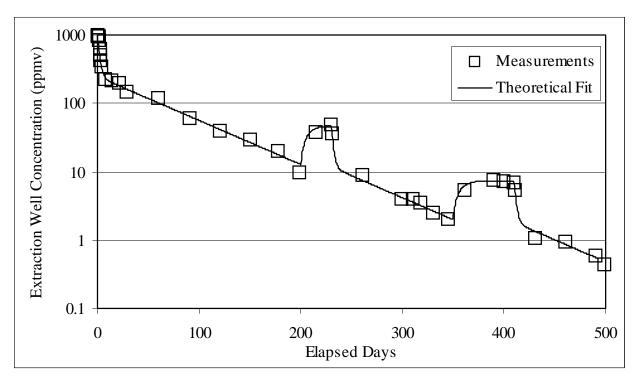


Figure F-1 Typical vapor concentration history during SVE with two rebound periods

In the example of Figure F-1, the extraction well concentration decays rapidly during the first two weeks of operation following an exponential trend. This period represents the time required to sweep the initial contaminant vapors found in the more permeable soil intervals. Beyond the first two weeks, the concentration decay follows a much slower exponential rate (i.e., notice the change in slope in the theoretical fit around Day 15). This slower rate corresponds to the rate of mass transfer from less permeable soils to more permeable soils. During this slower rate of decay, the process is often referred to as "asymptotic" with the asymptote being zero. In this example, a rebound period of 30 days was undertaken after 200 days of extraction to assess a hypothetical cleanup goal of 10 parts per million by volume (ppmv) throughout the site. Concentrations measured in the extraction well during this dormancy period revealed an increasing trend above the cleanup goal as contaminants diffused out of the less permeable soils and into the more permeable soils. Extraction was re-started at Day 230 before an equilibrium concentration had been reached. The concentration again decayed rapidly and the previous slow decay was re-established. A second rebound period was initiated at Day 350 and lasted 60 days. The 60-day period was sufficient to establish an equilibrium concentration less than the goal of 10 ppmv. The hypothetical system was operated an additional 90 days while closure reports were prepared and accepted. This example illustrates the simplest implementation and interpretation of SVE and rebound data. Many complexities arise when multiple extraction wells are operated, multiple contaminants are present, or the actual center of mass of the initial vapor plume is not known. The concepts in this appendix should provide a starting point for discussion and interpretation of results from more complex situations.

F-2. Theoretical Framework

As described in the previous section, soils are often divided into two categories for remediation: low permeability and high permeability, relative to each other. Early models of pump-and-treat referred to the relatively low permeability soil as "immobile" since the water in the soil was practically stagnant (see Brusseau, 1991 for a review). Recent work has applied the approach to soil vapor extraction (Kaleris and Croise, 1999) and air sparging (Rabideau and Blayden, 1998). The higher permeability soil is named "mobile" since the majority of flow occurs in these soils. In the vadose zone, the mobile soils are the most permeable and appreciable air flow through these soils is induced when a practical pressure gradient is applied (e.g., air injection or extraction in a well). Immobile soils have relatively low permeabilities and air flow through these soils during the application of a pressure gradient is considered negligible. Contaminant transport in immobile soils is dominated by diffusion in the vapor phase or liquid advection and diffusion if moisture contents are high.

As described in the previous example of SVE (see Figure F-1), the initial decay in contaminant concentration in the extraction well is governed by the transport of contaminants in flowing vapors through the mobile soils and is typically on the order of days or weeks. In the immobile soils, contaminant transport occurs on a time scale proportional to the diffusion rate and the length scale associated with the immobile soil (e.g., the thickness of a clay lens) and is typically on the order of months or years. Because of these disparate time scales, the concentration in the mobile soils (equivalent to the extracted concentration during SVE) falls much faster than the concentration in the immobile soils. Contaminant removal from the immobile soils relies on diffusion of contaminants to the interface with mobile soils where the contaminants are swept to extraction wells. Hence the concentrations in the mobile and immobile soils are in dis-equilibrium and define the macro-scale mass transfer constraint resulting from soil heterogeneities. This section develops mathematical relationships describing SVE using mass balances which can be employed to analyze rebound data and estimate field-scale mass transfer constraints. The mass transfer constraints for various physical phenomena and length scales are lumped into a single, average mass transfer coefficient assumed relatively constant over time.

Consider the total mass of contaminant, m_j , in a given volume, V, of soil type j where j can signify either "m" for mobile or "i" for immobile. The total contaminant mass in the soil is equal to the sum of the mass adsorbed, the mass dissolved in pore water, and the mass volatilized:

$$\begin{array}{l} m_{j} \, = \, C_{w,j} \, [\, (1 \! - \! \phi_{j}) \, \rho_{s,j} \, K_{d,j} \, + \, \phi_{j} \, S_{j} \, + \, \phi_{j} \, (1 \! - \! S_{j}) \, H] \, f_{j} \, V \\ \\ m_{j} \, = \, C_{v,j} \, \phi_{j} \, (1 \! - \! S_{j}) \, f_{j} \, V \, R_{j} \end{array} \tag{F-1}$$

The parameters are defined by:

 $C_{wi} = mass of contaminant per unit volume of pore water in soil type j$

 $C_{v,j} = \max$ of contaminant per unit volume of soil gas in soil type j

 $C_{v,j} = H C_{w,j}$ (Henry's Law)

 f_i = fraction of the treatment volume occupied by soil type j (NOTE: $f_m + f_i = 1$)

 ϕ_i = porosity of the soil in region j

 S_i = water saturation in region j

 $\rho_{s,j}$ = density of the solid matrix in region j

$$R_{j} = 1 + \frac{S_{j}\phi_{j} + \rho_{s,j}K_{d,j}(1 - \phi_{j})}{H(1 - S_{j})\phi_{j}}$$
 (F-2)

 $R_{\rm j}$ is the retardation factor for contaminant transport in the vapor phase and is analogous to the well-known retardation factor for contaminant transport in the liquid phase. H is the dimensionless Henry's constant for the contaminant under investigation at the soil temperature. $K_{\rm d,j}$ is the distribution coefficient of contaminants between the solid and liquid phases. These parameters are described in more detail in Chapter 3 of the Manual. This formulation assumes a NAPL is not present and surfaces of the soil grains are completely wetted by the pore water.

Removal of contaminants from the specified volume V during SVE or bioventing occurs by two major mechanisms. The first is by extracting the soil gases from the mobile regions and the second is degradation of the contaminants. In addition, as the concentration is reduced in the mobile region, contaminants diffuse from the immobile region into the mobile region. From a simple mass balance, the change in mass in the mobile fraction of the volume by these three mechanisms is described by:

$$\frac{dm_{m}}{dt} = -Q C_{v,m} - \gamma_{m} C_{w,m} S_{m} \phi_{m} f_{m} V + \alpha \phi_{i} (1 - S_{i}) f_{i} V (C_{v,i} - C_{v,m})$$
 (F-3)

In the immobile region, the change in mass is governed by:

$$\frac{dm_{i}}{dt} = -\gamma_{i} C_{w,i} S_{i} \phi_{i} f_{i} V - \alpha \phi_{i} (1 - S_{i}) f_{i} V (C_{v,i} - C_{v,m})$$
(F-4)

where:

Q = volumetric extraction rate of soil gases

t = time

 γ_i = degradation decay constant in region j

 α = first order mass transfer coefficient between the mobile and immobile regions

The first term in equation (F-3) represents the removal by pumping and the second term accounts for in situ degradation. The degradation is assumed to occur in the aqueous phase only. The third term accounts for mass transfer from the immobile regions into the mobile regions. The first term in equation (F-4) represents degradation in the pore water of the immobile region. The second term couples the transfer from the immobile region to the contaminant concentration in the mobile region. The transfer occurs only by diffusion in the vapor phase in this derivation, although equation (F-4) can be formulated to include liquid diffusion and advection if the water saturation is high in the immobile region.

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Equations describing the vapor concentrations in the mobile and immobile soils can be determined by substituting Equation (F-1) into (F-3) and (F-4):

$$R_{m} \frac{dC_{v,m}}{dt} = -\frac{Q}{\phi_{m}(1 - S_{m})f_{m}V}C_{v,m} - \frac{\gamma_{m}S_{m}}{(1 - S_{m})H}C_{v,m} + \frac{\phi_{i}(1 - S_{i})f_{i}}{\phi_{m}(1 - S_{m})f_{m}}\alpha(C_{v,i} - C_{v,m}) (F-5)$$

$$R_{i} \frac{dC_{v,i}}{dt} = -\frac{\gamma_{i}S_{i}}{(1 - S_{i})H}C_{v,i} - \alpha(C_{v,i} - C_{v,m})$$
 (F-6)

The initial decay rate shown in the example of Figure F-1, can be estimated from equation (F-5) and (F-6) can be used to estimate the "asymptotic" decay toward zero. During the initial extraction period, mass transfer from the immobile zone plays a small role and degradation generally takes much longer. Therefore, for the initial decay in concentration, equation (F-5) may be simplified:

$$R_{m} \frac{dC_{v,m}}{dt} = -\frac{Q}{\phi_{m} (1 - S_{m}) f_{m} V} C_{v,m}$$
 (F-7)

If the average initial concentration in the contaminated volume is designated as $C_{m,0}$, equation (F-7) may be solved to find,

$$C_{v,m} = C_{m,0} \exp\left(-\frac{Qt}{R_m V_m}\right) \tag{F-8}$$

where V_m [= $\phi_m (1-S_m) f_m V$] is the air-filled pore volume within the mobile fraction of the total contaminated volume. By fitting equation (F-8) to the initial observed decay in vapor concentration, an approximation for the mobile volume is obtained if the retardation coefficient is estimated from equation (F-2). This volumetric parameter will be employed in the evaluation of rebound data. Rearranging (F-8) and utilizing the initial condition yields,

$$\frac{Q}{R_{m}V_{m}} = \frac{1}{t_{measure}} ln \left(\frac{C_{m,0}}{C_{m,measure}} \right)$$
 (F-9)

where the subscript measure designates a time and concentration measurement before the mobile region has been fully swept. If the air-filled volume in the mobile zone can be estimated independently (e.g., from vapor monitoring wells and boring logs), then the time required for the initial flush of the mobile region by SVE can be determined from,

$$t_{\text{flush}} \approx \frac{R_{\text{m}} V_{\text{m}}}{Q} \ln(10) = \frac{2.3 R_{\text{m}} V_{\text{m}}}{Q}$$
 (F-10)

where the factor of ln(10) represents a decrease in concentration by one order of magnitude. After the initial flush of the mobile zone, the extracted concentration is determined primarily by the transport of contaminants from the immobile soil and the extraction rate. To simplify the discussion, assume degradation in the immobile soils is negligible. If we assume extraction from the mobile soils continues and that the extraction rate is sufficient to maintain the vapor concentration in the mobile zone much less than the concentration in the immobile soils, mass transfer from the immobile to the mobile soils can be estimated by:

$$R_{i} \frac{dC_{v,i}}{dt} = -\alpha C_{v,i}$$
 (F-11)

If the average initial concentration in the contaminated volume is designated as $C_{i,0}$, equation (F-11) may be solved to find an estimate for the average concentration in the immobile soil,

$$C_{v,i} = C_{i,0} \exp\left(-\frac{\alpha t}{R_i}\right)$$
 (F-12)

An expression for the vapor concentration in the mobile zone during the late period of soil vapor extraction can be estimated by substituting equation (F-12) into (F-5), again neglecting degradation for brevity of discussion,

$$R_{m} \frac{dC_{v,m}}{dt} + \frac{Q}{V_{m}} C_{v,m} = \frac{V_{i}}{V_{m}} \alpha C_{0,i} \exp\left(-\frac{\alpha}{R_{i}}t\right)$$
 (F-13)

The solution to this equation subject to an initial condition of C_{v,m}=0 at t=0 is,

$$C_{v,m} = C_{i,0} \frac{\alpha V_i}{R_m V_m} \left[\frac{Q}{R_m V_m} - \frac{\alpha}{R_i} \right]^{-1} \left[exp \left(-\frac{\alpha t}{R_i} \right) - exp \left(-\frac{Qt}{R_m V_m} \right) \right]$$
 (F-14)

The initial condition of zero for the mobile soil zone is valid at late times because the initial contamination in this region has been swept away. The volume parameter for the mobile region, V_m , is determined from the initial period of extraction as described previously and the volume parameter for the immobile region, V_i , can be estimated from soil properties and the expression:

$$V_{i} = \phi_{i} (1 - S_{i})(1 - f_{m})V = V_{m} \frac{\phi_{i} (1 - S_{i})(1 - f_{m})}{\phi_{m} (1 - S_{m})f_{m}}$$
(F-15)

If the retardation coefficients can be estimated, the only remaining unknown in (F-14) is the mass transfer coefficient, α . Therefore, fitting (F-14) to later extracted concentration data yields an estimate for the mass transfer coefficient. The mass transfer coefficient determines the rate of rebound and hence the anticipated dormancy period and the vapor sampling frequency to assess the vapor concentration in

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the low permeability regions. Setting Q=0 in (F-14) yields an estimate for the rebound in concentration in the mobile region,

$$C_{v,m} = C_{i,0} \frac{R_i V_i}{V_m} \left[1 - \exp\left(-\frac{\alpha t}{R_i}\right) \right]$$
 (F-16)

The characteristic timescale for the rebound concentration in the mobile soils to increase by one order of magnitude can be estimated by,

$$t_{\text{rebound}} \approx \frac{R_i}{\alpha} \ln(10) = \frac{2.3 R_i}{\alpha}$$
 (F-17)

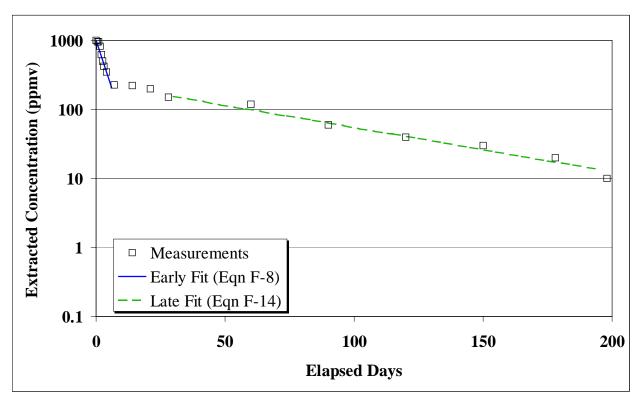


Figure F-2 Approximate equation fits to the example concentration history during SVE

The use of equations (F-8) and (F-14) is illustrated in Figure F-2 with the example data described previously. The slope of the early fit yields,

$$\frac{Q}{R_{\rm m}V_{\rm m}} = 0.26 \text{ days}^{-1}$$
 (F-18)

and the mobile volume parameter can be estimated if the extraction rate and retardation factor are available. The time scale for the initial flush as calculated with (F-10) is about nine days. Utilizing result (F-18) with (F-14), the best fit to the later data in Figure F-2 was achieved with the following mass transfer parameter,

$$\frac{\alpha}{R_i} = 0.073 \text{ days}^{-1}$$
 (F-19)

Variation of this parameter corresponded to changes in the <u>slope</u> for the fit while the initial concentration in the immobile region was varied to move the line up and down. The timescale for the rebound concentration to approach equilibrium can be calculated with (F-17). Using (F-19) an estimate of about 30 days is obtained.

F-3. Planning and Evaluation of Historical Data

The mathematical techniques presented in the previous section are only valid if the site is adequately characterized and the remedial system is appropriately designed. Before proceeding with a rebound test, answer the following questions:

- 1. Does the current site conceptual model or does existing site characterization data allow an estimate for the vadose zone heterogeneities in terms of the fraction which is mobile (e.g., sands) and the fraction which is immobile (e.g., silt or clays)? Have site-specific soil physical properties been measured?
- 2. Do concentrations measured in extraction wells and/or vapor monitoring points allow an estimate for the total volume of contaminated soil? Are the edges of the vapor plume defined? Is a reasonable estimate for the vertical distribution of contaminants available?
- 3. Has the concentration history in extraction wells exhibited a relatively rapid decay followed by a slow decay?

If the answer to (1) or (2) is generally "No" then additional investigative work may be warranted before or simultaneous with a rebound test. If the answer to (3) is "No" then it may be too early for a rebound test or the site may have additional complexities. For example, if very little decay occurs or a high concentration persists for a long period then NAPL may be present or the extraction wells may not be within the original source area. The impact of NAPL existence is to add another mass term to (F-1) and additional mass transfer terms to equations (F-3) and (F-4). As a result, the extraction well concentration would persist at a higher concentration than described previously and the decay would be much slower. If these types of complexities are suspected but not identified, then further investigative work should be undertaken prior to a rebound test. Methods of investigation are described in Chapter 3 of the manual. If the answers to all three are generally "Yes" then it is probably time for a rebound test.

Planning for a rebound test starts with an evaluation of historical data. The data of most interest are the extraction rates and the concentration histories at extraction wells. If these data are available, then estimates for the rebound period and vapor sampling frequency can be determined using the techniques described in the previous section. The steps are summarized below:

- 1. Plot the concentration on a log scale versus time
- 2. Fit a line through the initial decay using equation (F-8). The slope corresponds to Q/Rm/Vm while the line is moved up and down by varying Cm,0.
- 1. Fit a curve through the later slow decay using equation (F-14) and the fitted parameter Q/Rm/Vm. The general trend corresponds to /Ri while the curve is moved up and down by varying Ci,0.
- 4. Estimate the minimum rebound period using equation (F-17).
- 5. Specify vapor sampling times by plotting the anticipated concentration rebound using equation (F-16). A vapor sample collected about halfway between the final extracted concentration and the equilibrium rebound concentration is highly desirable to validate the fitted mass transfer parameter /Ri. This validation will provide strong evidence for an understanding of the site during the preparation of the closure report.

After evaluating the historical data and estimating time scales, a Work Plan should be prepared for the performance of the rebound test. A well thought out and well written Work Plan as described in Paragraph 4-4 of the Manual is a key element in the success of the test. Just as important is the communication of the Work Plan to field personnel.

The first step in preparing the Work Plan is to set objectives. For rebound testing, the primary objectives are to measure the residual vapor concentrations in low permeability soils and to identify locations with high residual concentrations. With these data and estimates for the contaminated volume, the total residual mass in the site subsurface can be evaluated. If the residual mass is relatively low the site can be closed. If cleanup goals have not been met then future system operation can be optimized to meet the goals.

The following list of tasks summarizes the planning stage of a rebound test:

- 1. Compile historical data
 - a. Extraction rate history
 - b. Extracted vapor concentration history
 - c. Monitoring point vapor concentration history
- 2. Evaluate characterization and historical data
 - a. Is the site sufficiently characterized to estimate the degree of heterogeneity and the contaminated volume?
 - b. Estimate representative contaminated volume
 - c. Estimate overall mass transfer coefficient
 - d. Is a rebound test useful at this point? Is the extracted concentration low and slowly decaying?
- 3. Set objectives for the effort
 - a. Estimate residual mass
 - b. Locate residual mass
 - c. Estimate duration of operation to meet cleanup goals (or provide data for risk assessment modeling to close the site)
- 4. Specify parameters for measurement and sampling frequencies
 - a. Vapor concentrations in extraction wells prior to the start of the rebound test
 - b. Vapor concentration decay in extraction wells
 - c. Extraction rates
- 5. Prepare the Work Plan

F-4. Field Procedures

The execution of a rebound test occurs in three phases: (1) steady operation and monitoring of the SVE system, (2) shutdown for a period of dormancy, and (3) re-start of the SVE system. The extraction period leading up to the rebound test should be performed with as few disruptions as possible. At sites with multiple extraction wells, different extraction strategies are often employed to maximize contaminant recovery and to avoid stagnation zones. In the period leading up to the rebound test, a single extraction configuration should be employed to avoid complexities in the data interpretation.

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Several rounds of vapor sampling should be performed at normal intervals (e.g., monthly) to define the slow decay in the existing extraction configuration.

After several rounds of sampling yield consistent decay curves, the rebound test may be initiated. This phase begins by collecting a final round of vapor samples along with measurements of total concentration using field portable instruments such as a PID or FID, as appropriate. After collecting the samples and measurements, the extraction wells are closed and the extraction pumps are turned off. Care should be taken to minimize the flow of atmospheric air through the wells and into the subsurface. All extraction wells and monitoring points should be capped. The site should then be left undisturbed except for vapor sampling as specified in the Work Plan. Vapor sampling during the dormant period is best performed with a small sampling pump, if possible. The well being sampled should be purged by extracting a volume equivalent to at least three volumes of the well casing and screen. In addition, a field portable PID or FID should be used to monitor the extracted vapors to ensure a relatively steady concentration has been reached before the vapor sample for detailed analysis is collected. If the vapor sampling during the dormant period yields a clear trend to an equilibrium concentration, the system may be re-started. In past practice it was common to allow the rebound period to be "long" to ensure the site re-equilibrated before re-starting extraction. No samples were collected during the rebound period since the only parameter of interest was the equilibrated concentration. However, without sampling during the rebound period, no data will exist to demonstrate re-equilibration and a valuable assessment of the mass transfer rate between mobile and immobile soils is lost.

The final period of the rebound test is the system re-start. Just prior to starting the extraction system, a round of vapor sampling should be performed to define the endpoint of the rebound. The re-start of extraction should be in the same configuration and at the same rates as the steady period leading up to the rebound period. With the same configuration, the extraction well vapor concentrations before and after the rebound period are directly comparable. Vapor sampling during the period immediately following the re-start is critical. The maximum rebound concentration may or may not appear at the extraction wells immediately after re-start. Recall the previous discussion on the distribution of contaminants. If the extraction wells are not located in the middle of the contaminant mass, the concentration may rise for a short period before the decay associated with the sweep of the mobile soils begins. Therefore, the extracted vapors should be monitored with a field portable PID or FID during the initial hours of extraction. A vapor sample should be collected for analyses at or just after a peak is observed. If the initial concentration is the maximum and decay begins immediately, then the final rebound sample is representative of the initial extracted concentration. The goal of the vapor sampling during the re-start is to define the decay trend associated with the sweep of the mobile soils and the subsequent slower decay as the removal becomes diffusion limited. It is expected that the diffusionlimited trend will return to the decay rate observed just before the rebound period.

F-5. Data Evaluation

As described in Section F-2, analyses of the early and late concentration trends can yield estimates for the total contaminated volume and the field mass transfer coefficient. However, the objectives of a rebound test are to assess the mass of residual contamination and concentrations within low permeability materials. This section presents mathematical relationships to estimate the residual contaminant mass at a site using the data from a rebound test. Measures of vapor concentrations in the low permeability soils come directly from the rebound data. The mathematical analysis assumes the following data are available after following the field procedures described in the previous section,

- 1. Analyses of extracted vapors defining the decay trend prior to the initiation of the rebound test and the extraction rate during this period;
- 2. Measures of mobile soil concentrations during rebound up to equilibrium with the immobile soils; and
- 3. Analyses of extracted vapors defining the decay trend during extraction after the rebound test and the extraction rate.

Equations describing volume-averaged vapor concentrations in the mobile and immobile soils were presented in Section F-2 as equations (F-5) and (F-6). These equations were simplified under various assumptions to yield straightforward relationships for evaluating trends in the extracted concentration. However, the equation pair can be solved exactly given an initial concentration in each soil region. Equations (F-5) and (F-6) represent coupled, first-order, ordinary differential equations for the vapor concentrations. If the extraction rate Q and the mass transfer coefficient α are constant, coefficients in both equations are constant and the solution is easy to obtain. If the extraction rate varies, such as the dormancy period during rebound, then the equations can be solved piecewise using the volume-averaged concentration in each region at the end of a constant extraction rate period as the initial condition for the next constant extraction rate period. Solving the equations in terms of the vapor concentrations and designating the initial average vapor contaminant concentration in each region as $C_{m,0}$ and $C_{i,0}$ at some initial time t_0 yields:

$$C_{v,m} = \Omega_1 \exp[r_1(t - t_0)] + \Omega_2 \exp[r_2(t - t_0)]$$
 (F-20)

$$C_{v,i} = \Omega_1 \omega_1 \exp[r_1(t - t_0)] + \Omega_2 \omega_2 \exp[r_2(t - t_0)]$$
 (F-21)

where:

$$\Omega_1 = \frac{C_{i,0} - \omega_2 C_{m,0}}{\omega_1 - \omega_2}$$

$$\Omega_2 = \frac{\omega_1 C_{m,0} - C_{i,0}}{\omega_1 - \omega_2}$$

$$\omega_1 = \frac{R_m r_1 + \Theta + \alpha \Phi}{\alpha \Phi}$$

$$\omega_2 \; = \; \frac{R_m r_2 + \Theta + \alpha \Phi}{\alpha \Phi}$$

$$\Theta = \frac{Q}{V_{m}} + \frac{\gamma_{m} S_{m}}{H(1 - S_{m})}$$

$$\Phi = \frac{V_{i}}{V_{m}} = \frac{(1 - f_{m})\phi_{i}(1 - S_{i})V}{f_{m}\phi_{m}(1 - S_{m})V}$$

$$\Gamma = \frac{\gamma_i S_i}{H(1-S_i)}$$

$$r_{1} = \frac{-b + \sqrt{b^{2} - 4R_{m}R_{i}[\Gamma(\Theta + \Phi\alpha) + \Theta\alpha]}}{2R_{m}R_{i}}$$

$$r_2 = \frac{-b - \sqrt{b^2 - 4R_m R_i \left[\Gamma(\Theta + \Phi\alpha) + \Theta\alpha\right]}}{2R_m R_i}$$

$$b = R_m(\alpha + \Gamma) + R_i(\Theta + \Phi\alpha)$$

Equations (F-20) and (F-21) are simple to use for matching contaminant extraction concentrations for a given extraction history. Early data may not fit well because the initial distribution of contaminants at field sites is generally very different than the uniform, average concentration assumed by the theoretical formulation. However, after the initial sweep of the mobile soils, the concentration history is generally well-behaved and approaches an average concentration because of mechanical dispersion (i.e., advective mixing). The equations provide an accurate engineering model for predicting site behavior in the later mass-transfer-limited phase if complicating factors do not exist (e.g., NAPL).

Because of the volume averaging over each soil region, very few parameters appear in the equations relative to the input required for detailed numerical modeling of an SVE system. The input and/or fitting variables are,

This list of variables is very similar to the parameters used in two-region modeling of solute transport in saturated systems (Griffioen et al., 1998). Average soil physical properties in each region such as porosity and water saturation are usually available from independent measurements. With these soil physical properties and Henry's constant for the contaminant, the retardation coefficient in each region can be estimated as described in Chapter 2. If degradation of the contaminant is considered significant, the degradation coefficient could be estimated from the appearance of daughter compounds in the extracted vapors; however, such an analysis is beyond the scope of this document. By definition the concentration in extracted vapors is equal to the concentration in the mobile soils. Therefore, the measured extraction concentration at a specified start time t_0 is the initial concentration in the mobile

region. Fitting SVE and rebound concentration data generally requires varying only four parameters in equation (F-20): $C_{i,0}$, V, f_m and α . Case studies of site-specific parameter fitting are presented in the next section.

After fitting equation (F-20) to a series of extraction well concentrations associated with a rebound test, values for the fitted parameters can be checked for consistency with other existing data. Vapor concentrations are often measured in monitoring points constructed in the vadose zone around extraction wells. The monitoring points are frequently installed in low permeability soils which correspond to the immobile soil region. These measured concentrations at the start of a rebound period should correspond roughly to the fitted average initial concentration in the immobile region. Data from a number of monitoring points can be used to calculate an order-of-magnitude estimate for the total contaminated volume. This volume can be compared with the fitted representative volume. A review of boring logs or vertical flow profiles from PneuLog® can also yield an estimate for the fraction of soil which is mobile. For example, a site with distinct sand and silt intervals would only require an estimate for the total thickness of sand divided by the total thickness of the vadose zone to arrive at an estimated mobile fraction in the soil for comparison with the fitted fraction. Finally, the mass transfer coefficient can be estimated from vaporous diffusion theory in a slab. Again, a review of well logs may reveal an average thickness for immobile soil regions (e.g., thin clays or thick moist silts interbedded in sands) and previous measurements may yield the water saturation. Looking at the leading term in the linear diffusion solution leads to the following estimate for the mass transfer coefficient,

$$\alpha \approx \frac{D \phi_i^{4/3} (1 - S_i)^{10/3} \pi^2}{R_i a^2}$$
 (F-22)

where D is the vapor phase diffusion coefficient of the contaminant in free air and a is the half-length over which diffusion occurs (i.e., half the thickness of typical immobile region intervals). The fitted and calculated mass transfer coefficients should be of the same order of magnitude.

As stated above, one of the goals of the rebound test is to evaluate the mass of contaminant remaining in the subsurface. After fitting the model above to the concentrations observed with the rebound test, equation (F-1) can be used to generate an order-of-magnitude estimate for the total residual contaminant mass,

$$m_{total} = m_m + m_i = C_{v,m} R_m \phi_m (1-S_m) f_m V + C_{v,i} R_i \phi_i (1-S_i) (1-f_m) V$$
 (F-23)

If the field conditions are adequately modeled by the two-region concept and the fitted parameters are consistent with other information, then the model of the rebound data yields powerful information regarding closure or optimization of the existing system. For example, the calculations may yield estimates for a small residual mass and/or the attainment of cleanup goals. For optimization, the model can predict durations of extraction to reach cleanup goals for various extraction rates.

F-6. Case Studies

This section presents two case studies for the evaluation of SVE and rebound concentration data using the mathematical models described in this appendix. Both sites are located in California's Central

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Valley and both were contaminated with TCE and PCE. The first example is a relatively simple site where two extraction wells were operated simultaneously for nearly two years at a steady flow rate with a number of shutdown periods. Vapor sampling was performed only with the combined flow. Individual wells were not sampled. The second example is from a more complicated site where from one to four wells were operated simultaneously in various configurations with varying extraction rates and two rebound tests over a five year period. Modeling of this more complicated site required a detailed review of extraction rates, durations, and measured concentrations from both individual wells and the combined flow in the manifold.

a. Case Study Site 1

Historical operation of SVE at Site 1 was simultaneous extraction from two wells without any flow balancing (i.e., the same vacuum was applied to both wells). In addition, only total flow was measured and all extracted concentrations were collected from the combined vapor stream. Therefore, historical data do not exist for the concentrations and masses removed from individual wells. The historical TCE concentrations measured in the combined stream during the first year and half of SVE at Site 1 are illustrated in Figure F-3. Startup of the system involved a couple of brief shutdowns and a long shutdown occurred after the first month. The system was re-started during the ninth month. The extraction history used to model the process consisted of 69 constant flow segments but these were generally either 400 cubic feet per minute or zero. The extraction rates, start times and stop times were estimated from monthly status reports. The assumed soil properties for the modeling are listed in Table F-1. K_d was set equal to one because organic carbon was not detected in any soil samples from the site.

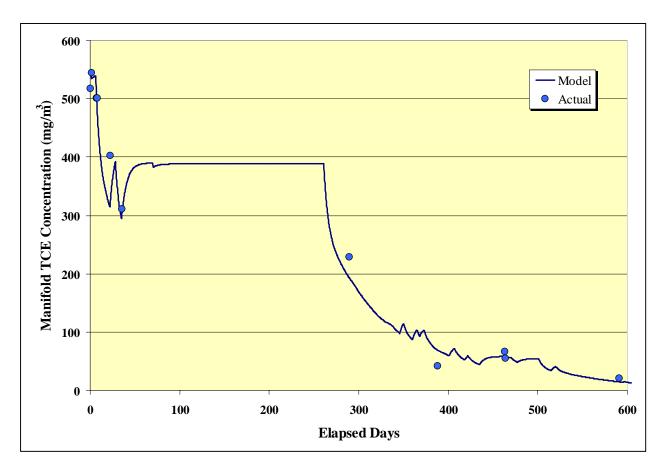


Figure F-3 Summary of historical TCE concentration measurements

Table F-1.				
Input Parameters Yielding the Best Fit of the SVE System Manifold Concentrations				
Soil Property	Units ^a	Mobile Zone	Immobile Zone	
Initial Vapor Concentration	mg/m ³	545	545	
Porosity	ND	0.487	0.487	
Water Saturation	ND	0.25	0.40	
Grain Density	kg/m ³	2.66	2.66	
Characteristic Thickness	m	-	0.4	
Characteristic Volume	m^3	288,100	864,200	
K _d	L/kg	0	0	
Degradation Rate	1/yr	0	0	
TCE Properties				
Henry's Constant	ND	0.38		
Octanol-Water Partition	ND	200		
Diffusion Coefficient in Air	m ² /day	0.68		

 $^{{}^{}a}ND = dimensionless$

The two-region model provided a good match to the historical manifold TCE concentration. As described in Section F-5, the model was run varying the initial soil vapor concentration, the total contaminated volume, the percentage of the subsurface categorized as mobile, and the mass transfer coefficient between mobile and immobile zones. The best-fit values are listed in Table F-1. The total characteristic volume was estimated to be 40,690,000 cubic feet (1,152,300 cubic meters). Of this total volume, 25% was represented as mobile and 75% as immobile. For a vadose zone thickness of 80 feet (24.4 m), the characteristic radius was 400 feet (123 m) equivalent to a surface area of about 12 acres. This total characteristic volume was consistent with the flow observations from PneuLog® and the vacuum responses at monitoring points. The two wells influenced a very large area because they intersected a permeable sand channel near the bottom of the vadose zone. In addition, usage history indicated a number of possible release points for contaminants existed across the site. Using the initial estimated vapor concentration of 545 mg/m³, the best-fit total volume yields an estimated total original mass for TCE of 1,074 pounds (487 kg). The overall mass transfer coefficient between the mobile and immobile soils was estimated to be 0.108 day¹ corresponding to a time scale of 9 days. This suggests rebound during shutdown periods was relatively rapid.

The calibrated two-region model developed by matching the historical data for the combined extraction was used to forecast future performance. Model predictions for the combined concentration and cumulative mass removed are presented in Figure F-4. The model forecasts reaching an equivalent TCE concentration of MCL in the pore water of the immobile soils around day 800.

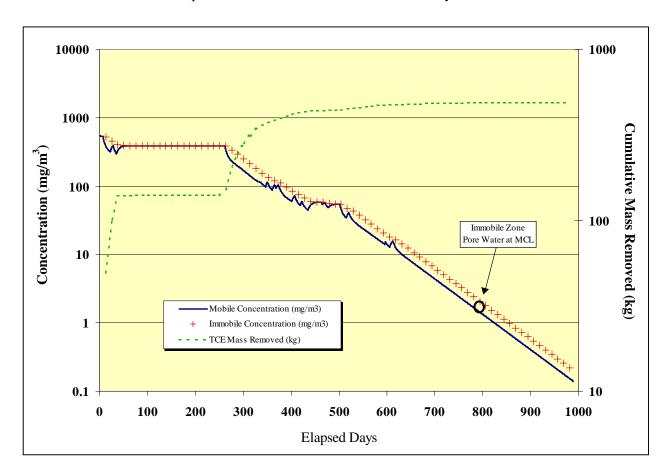


Figure F-4 Forecast for continued operation of the existing SVE system

b. Case Study Site 2

Site 2 is located in the Central Valley of California. The subsurface at Site 2 readily meets the conceptual model of mobile and immobile zones for air movement during SVE. PneuLog® flow profiles revealed only about 20 % of the vadose zone allowed effective air flow. These mobile zones consisted of interbedded sand layers within an immobile zone predominantly made up of moist silts and fine sands. Historical concentration and flow data were available from both the manifold (representing the cumulative extraction rate from all wells and the mixed contaminant concentrations), individual extraction wells, and vapor monitoring wells. The history shows the concentrations rising during the first week of operation. After this initial period, both the TCE and PCE concentrations exhibited the classic exponential decay. The initial 90 days of extraction were performed with a single extraction well (VW-01) near the center of the suspected source area. This 90-day period was followed by additions and modifications to the extraction configuration using three other surrounding wells and two rebound periods.

The two-region model was applied using soil properties measured at the site and a detailed extraction history employing 193 constant flow segments over a four-year period to fit the observed PCE concentrations in the manifold and from well VW-01. The procedure followed to fit the data is outlined in Section F-5. The resulting model fits are illustrated in Figures F-5 and F-6. Similar results were achieved for TCE data. The initial concentration in the mobile phase was assumed equal to the early (day 9) peak concentration observed in the manifold. The other best-fit values for PCE are listed in Table F-3. The total characteristic volume of contaminated soil was estimated to be 1,099,400 cubic yards (840,600 m³) with roughly 18 % characterized as mobile and 82 % immobile. For a depth to groundwater of 105 feet this yields an equivalent radius of 300 feet for the contamination. This radius correlated well with the overall dimensions of observed PCE contamination at the start of remediation. The characteristic diffusion length estimated for the immobile zone was about 1.15 feet (0.35 m) corresponding to an average total thickness of about 2.3 feet for each immobile zone region. This characteristic length was calculated using equation (F-22) and the fit mass transfer coefficient. In addition, this length is consistent with the observations from the PneuLog® flow profiles. The best-fit immobile zone initial vapor concentration (565 ppmv) was equivalent to the mobile zone (650 ppmv) indicating the mobile and immobile regions were in equilibrium. The values differ because differing soil properties yield differing partitioning components. Using the estimated initial mobile and immobile zone PCE vapor concentrations and the best-fit total volume yielded an estimated total initial mass for PCE of 4,130 pounds (1,873 kg).

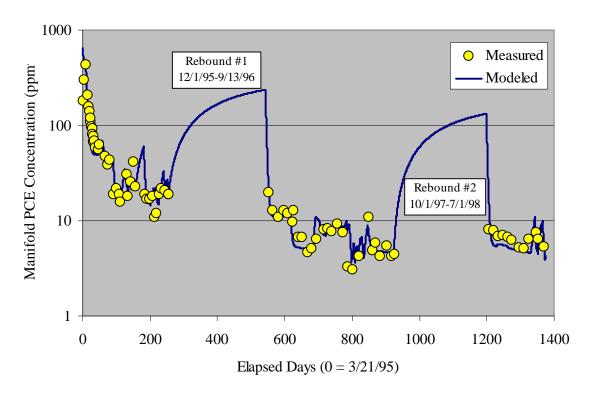


Figure F-5 Measured and modeled PCE vapor concentrations at the manifold

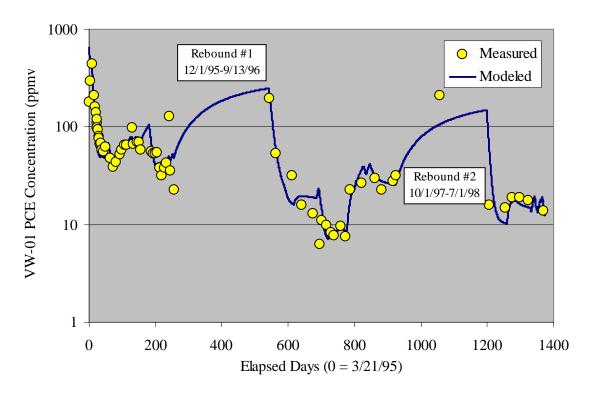


Figure F-6 Measured and modeled PCE vapor concentrations in well VW-01

Table F-2.				
Parameters for Modeling PCE Removal at Site 2				
Soil Property	Units ^a	Mobile Zone	Immobile Zone	
Initial Vapor Concentration	ppmV	650	565	
Porosity	ND	0.473	0.507	
Moisture Content (vol)	ND	0.080	0.343	
Grain Density	g/cm ³	2.65	2.65	
Characteristic Thickness	m	-	0.35	
Characteristic Volume	m^3	151,300	689,265	
K _d	L/kg	0.018	0.072	
Degradation Rate	1/yr	0	0	
PCE Properties				
Henry's Constant	ND	1.10		
Octanol-Water Partition	ND	600		
Diffusion Coefficient in Air	m ² /day	0.63		

^a ND = dimensionless

With a calibrated model of site behavior during SVE, forecasts of future performance were possible and residual mass and concentration estimates could be compared with cleanup goals. Predicted future performance at the site is illustrated in Figure F-7 where the operation of two wells was found to be the optimum. The forecasted, optimized operating time to reduce the average PCE vapor concentration in the immobile zone to 10 ppmv is about 28 months beyond the operations at the time of modeling. The residual PCE mass at 10 ppmv is estimated to be 61 pounds. To reach an average of 1 ppmv in the immobile zone, extraction must continue another 20 months. At this end, the residual PCE mass is estimated to be 6 pounds.

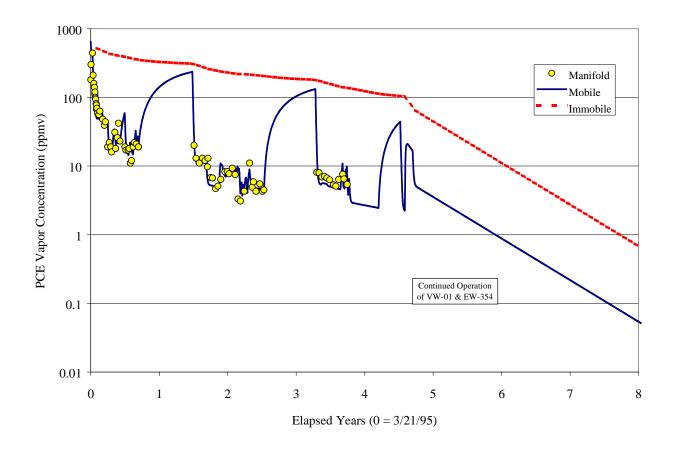


Figure F-7 Forecast for PCE removal using optimized extraction well configuration.

F-7. References

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